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IMPROVED U/PU SEPARATION IN PULSED COLUMNS BY OPTIMIZED PULSATION CONDITIONS AND USE OF TWO CONSECUTIVE EXTRACTION COLUMNS

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ABSTRACT

The separation of plutonium from uranium in the PUREX process was investigated in a pulsed column facility. The separation efficiency can be improved by optimization of the pulse conditions.

A further essential improvement was achieved by use of two consecutive electroreduction pulse columns. With this equipment excellent decontamination factors for Pu up to 500000 were measured and so the specification of the final uranium product was met in only one step. The required separation of the uranium from the plutonium product was achieved by a scrub part integrated in the first electroreduction column.

INTRODUCTION

In the PUREX process plutonium is normally separated from uranium after both constituents have been extracted into the organic extractant (30 vol. % tri-n-butyl phosphate in n-alkane).

The extracted tetravalent plutonium is reduced to Pu(III) and backextracted into an aqueous nitric acid solution. During that process most of the uranium is left in the organic phase. The most commonly used reductant is U(IV), which is prepared either outside the contactor and then supplied to it or, as in the electroreduction method developed in Karlsruhe, produced within the contactor.

In the majority of reprocessing plants serving civil purposes, U/Pu separation is performed in mixersettlers. Relatively little experience with pulsed columns has been published. The available data have been accumulated mainly at the Eurochemic plant at Mol (1), the Dounreay testing facility and in experiments performed in PUTE [1] in Karlsruhe (2, 3, 4). Decontamination factors of up to 2000 for plutonium have been achieved in PUTE. These are sufficient for a PUREX process comprising three cycles, but they are much lower than theoretical expectations.

As our activities have been directed to optimizing the individual steps of the PUREX process to such an extent that only one single extraction cycle yields the necessary product specifications (5), the separation efficiency had to be markedly improved.

OPTIMIZATION OF THE PULSATION PARAMETERS

The first experiments on U/Pu separation in PUTE were performed in an electro-reduction column made of titanium (6) which had been successfully used to demonstrate plutonium backextraction in the plutonium purification cycles of the PUREX process. Decontamination factors (DF´s) of nearly one million had been achieved for plutonium (2, 7), so we anticipated DF´s also for U/Pu separation much higher than 2000. As the tests were performed in a metal column, a visual observation of the events taking place was not possible. The Pu an H^+ concentrations which have been measured in U/Pu separation (Fig. 1) show very flat profiles with a clear jump in plutonium concentration in the organic phase above the top decanter of the column. We have concluded from this finding that the aqueous phase rich in plutonium has been entrained, enclosed in organic droplets, from the bottom part of the column into the top part. When the organic droplets coalesce at the phase boundary in the top decanter the entrained aqueous phase is released, which causes the jump in plutonium concentration of the organic phase in the decanter.

In order to better study this effect, a second electro-reduction column for U/Pu separation was installed in PUTE. The new column was built with a glass jacket to facilitate observation of the dispersion. In addition the column was equipped with a remote head membrane pulsator admitting higher pulsation frequencies (up to 160/min) than the air pulsators used in the other columns in PUTE (up to 90/min). The flowsheet of the experiments is shown in Fig. 2.

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[1] PUTE = plutonium test facility of 100 kg U + Pu/l capacity

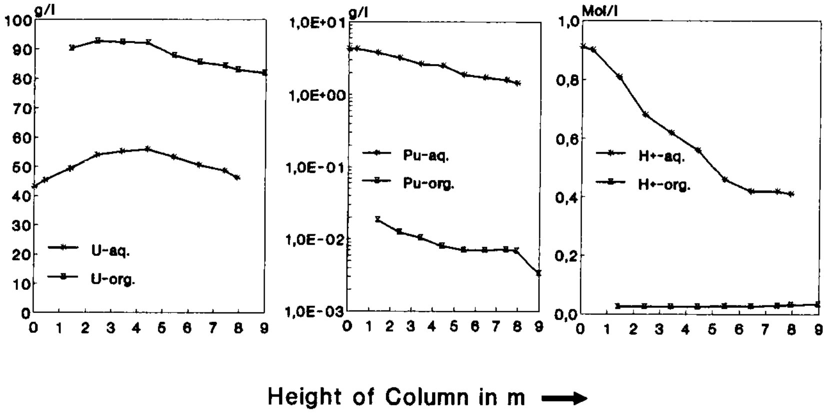

Fig. 1: Typical concentration profiles of 1BX electroreduction column in former experiments (Ti-column)

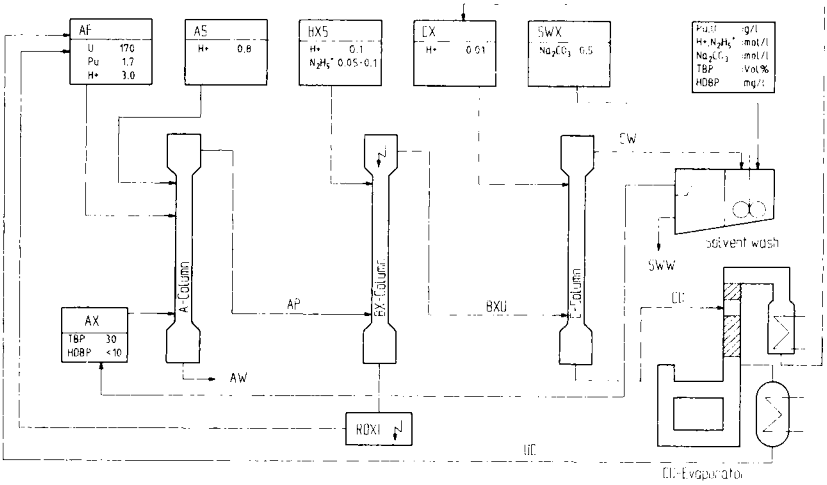

Fig. 2: Plutonium test facility PUTE
Flowsheet for optimized U/Pu separation by electroreduction

The aqueous nitric acid, uranium, and plutonium containing feed solution is introduced into the upper third of the extraction column, where it contacts the organic extractant in a countercurrent flow. Uranium and plutonium are extracted into the organic phase and scrubbed in the upper third of the column with fresh diluted nitric acid. The desired heavy metal loading of the extractant is set by the ratio of flow in the extraction column, i. e. the volumetric flow rate of the aqueous feed solution, with the extractant flow defined in advance.

The loaded extractant is subsequently fed into the bottom part of the electrolytically operated U/Pu partitioning column. In the partitioning column some of the U(VI) is reduced at the cathode to U(IV) which then quickly reduces Pu(IV) to Pu(III). The practically non-extractable Pu(III) is transferred into the aqueous phase during that process. Hydrazine nitrate is added to the nitric acid solution used for backextraction to stabilize the trivalent plutonium.

The aqueous Pu product solution from the electrolytic column is then fed into an electro-oxidation cell (ROXI) in order to reoxidize the hydrazine to nitrogen and Pu(III) to Pu(IV). To close the plutonium cycle the Pu(IV) solution is then returned to the feed solution tank. The organic extractant, which is largely free of plutonium but contains most of the uranium, is discharged at the head of the partitioning column. The uranium is backextracted into the aqueous phase in the third column (1C column) using highly diluted nitric acid, subsequently concentrated and, in order to close the uranium cycle, likewise recycled into the feed solution tank. The evaporator distillate is used again for uranium backextraction.

The extractant, now free of uranium and plutonium, is discharged from the uranium backextraction column and scrubbed in a single stage mixer-settler with soda solution in order to eliminate radiolytic products which would interfere with the subsequent operation of the process. The scrubbed extractant is then recycled upstream of the extraction column.

The results to the first tests performed with the glass column were compared with those of the tests previously performed with the titanium column. The measured DF of plutonium of 268 is lower by approx. a factor of 5 than the DF measured under comparable operating conditions in the titanium column (Fig. 3). A comparison of the measured concentration profiles shows that this is attributable to the 6 m extraction length of the newly installed glass column which is shorter by 1.6 m than that of the titanium column. In that test the supposed entrainment of the aqueous phase along with the organic droplets became visible for the first time. Figure 4a shows the dispersion in the central part of the column. It is clearly visible how aqueous droplets are enclosed in large organic droplets and are carried from the bottom part of the column to the top. These results provided experimental confirmation of the proposed reason for the previously measured relatively low decontamination factors for plutonium. An additioned goal of these experiments was to determine how to avoid this effect by variation of the operating parameters. With the other conditions remaining constant, the following parameters were varied:

- the volume flow rate in the range from 50-80 % of the flooding capacity;
- the temperature in the range from 25 °C to 45 °C;

- the heavy metal loading of the organic feed solution in the range from 65 g/l to 90 g/l;
- the acid concentration of the aqueous backextraction solution in the range from 0.1 molar to 0.3 molar.

Pulse Energy [cm/min]	Extraction height for Pu strip (BX) [m]	$[Pu]_{BXU}$ [mg/l]	Pu - DF	Visual Appearance of Dispersion
90	7.6	0.63	1350	not observed (TI-Column)
90	6	2.75	268	large organic drops, many inclusions of aqueuos phase
140	6	1.30	692	smaller organic drops, some inclusions of aqueuos phase
180	5	0.06	11900	*small organic drops form* a homogeneous dispersion, no inclusions of aqueuos phase

org. feed : 89 to 92 gU+Pu/l, [U]/[Pu] ~100, $[HNO_3]$ ~ 0.2 M
strip solution : $[HNO_3]$ = 0.1 M, $[N_2H_5^+]$ = 0.05 to 0.1 M
volume flow ratio org. / aq. in BX part : 5 to 6
cathodic current density : 0.5 to 3 mA/cm^2

Fig. 3: U/Pu separation results achieved with electroreduction pulsed columns in PUTE facility

None of these parametric changes had a substantial influence on the quality of dispersion in the column or on the measured decontamination factors for plutonium. However, it appeared that the point of origin of the great organic phase droplets with the aqueous droplets enclosed shifted with changes in acid concentration. It can be seen from the measured concentration profiles that this is always the point where the maximum uranium concentrations occur, i. e. the direction of uranium material transfer is reversed. Therefore we suppose that instabilities arise due to the change in direction of material transfer and inclusions of aqueouse foreign phase develop.

Another operating parameter subjected to variations was the pulsation energy (expressed as the product of pulsation amplitude and pulsation frequency), which was increased from the standard value of 90 cm/min to 180 cm/min. As pulsation energy increased smaller organic droplets containing less aqueous foreign phase were produced (Fig. 4). At 180 cm/min pulsation energy, no entrainment was visible and, accordingly, decontamination factors for plutonium of greater than 10,000 were achieved (Fig. 3). The measured concentration profiles (Fig. 5) clearly

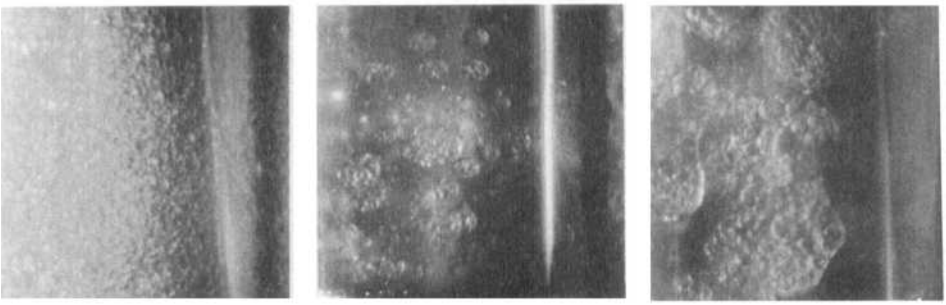

Fig. 4: Dispersion in 1BX column as function of pulse energy
left: 90 cm/min; middle: 140 cm/min; right: 180 cm/min

show a steeper slope than in previous experiments (Fig. 1) However, enhancing the separation efficiency in this way requires operation of the column in the range of lower volume flow rates. The flooding capacity is reduced by approx. one third (Fig. 6), so the column diameter must be increased by about 20 % for the throughput to remain the same.

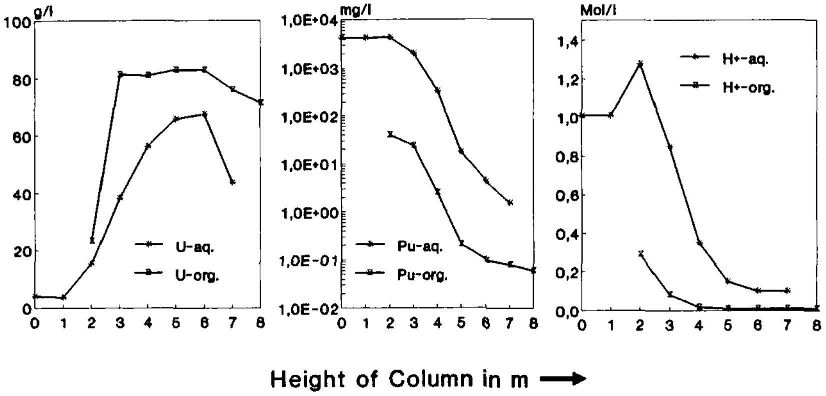

Fig. 5: Concentration profile of 1BX electroreduction column by optimized pulse conditions

USE OF TWO SERIES-CONNECTED PARTITIONING COLUMNS

In further tests both electro-reduction columns were series-connected for U/Pu separation (Fig. 7). The upper 6.6 m of the titanium column were used as the BX1 part (U/Pu separation) and the lowest 1 m long section of the column was used as BS part for uranium backwash from the aqueous Pu product solution. The glass column of 6 m extraction length was series-connected for plutonium fine separation (BX2).

The aqueous backextraction solution, which contained hydrazine, was fed into the BX2 column at the head of the column and the aqueous discharge

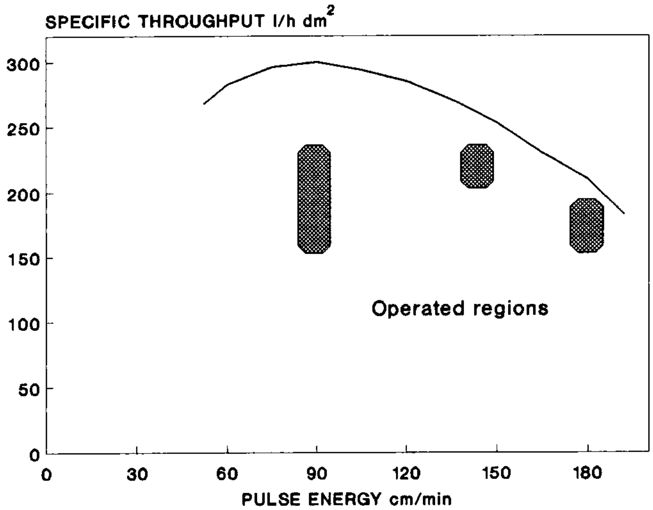

Fig. 6: Flooding diagram of 1BX electroreduction column as function of pulse energy

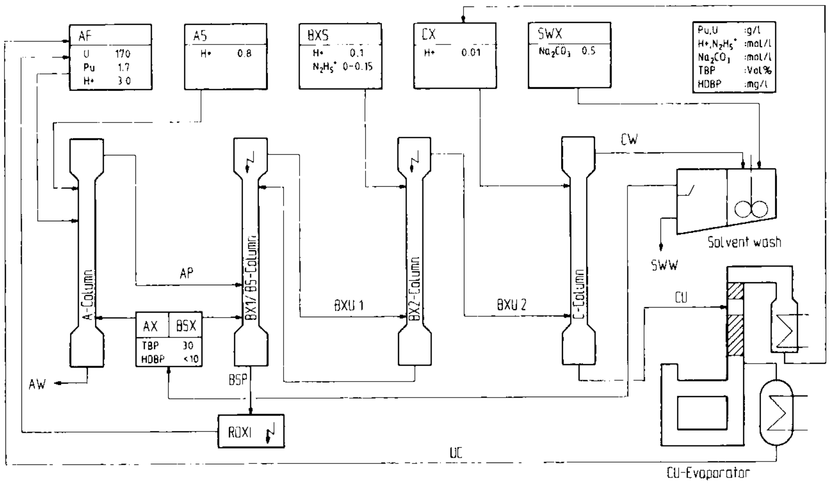

Fig. 7: Plutonium test facility PUTE
Flowsheet by use of two consecutiv electroreduction columns

of this column was returned into the BX1 column. Because of the differences in pulsation systems, it was not possible to operate the titanium column at other than 135 cm/min pulsation energy, whereas in the series-connected glass column the optimized pulsation energy of 180 cm/min was used. During these tests the organic to aqueous flow ratio in the 1BX part was increased, i. e. from 6 to 9.33 (Fig. 8). In the first test involving a flow ratio of 6 in the 1BX part a residual plutonium concentration of less than 0.01 mg Pu/l was attained in the organic raffinate of the second column. Subsequently, the analysis was performed with an improved detection sensitivity. For a flow ratio of 7.25, a plutonium residual concentration of only 1.5 µg Pu/l in the organic raffinate was detected. From this a total plutonium DF across the two columns of greater than 500,00 can be calculated. Thus, the plutonium specification for the uranium product was attained in a single extraction cycle. When the flow ratio was increased to 9.33, DF's for plutonium of greater than 100,000 were still achieved.

Volume flow ratio org./aq. in BX part	Pulse energy		$[Pu]_{BXU2}$ [mg/l]	Pu - DF	U - DF
	1. column [cm/min]	2. column [cm/min]			
6	135	180	«0.01	»73000	143
7.25	135	180	0.0015	507000	345
9.33	135	180	0.005	116000	311

org. feed : 88 to 90 gU+Pu/l, [U]/[Pu] ~ 100, $[HNO_3]$ ~ 0.2 M
strip solution : $[HNO_3]$ = 0.1 M, $[N_2H_5^+]$ = 0.05 to 0.15 M
extraction height : BX part : 6.6 m • 6 m
BS part : 1 m
volume flow ratio org./aq. in BS part : 1
cathodic current density : 0.5 to 0.8 mA/cm^2

Fig. 8: U/Pu separations results achieved by use of two consecutive electroreduction columns

The 1 m BS part of the column, which was integrated in the U/Pu partitioning column, proved to be extremely effective. It allowed the reduction of the U/Pu ratio in the Pu product from about 10 to less than 1. Such a high degree of separation of uranium from the plutonium product is completely sufficient, at least for a PUREX process consisting of three cycles, and it is optimum if plutonium backextraction by electroreduction is used in the purification cycles.

BEHAVIOR UNDER FAILURE CONDITIONS

In a further test the behavior under failure conditions (maloperation) of the interconnected two columns was investigated. The loss of stabilizer was simulated by feeding the solution used for backextraction into the column with no hydrazine added. At the end of 12 hours hydrazine had been depleted from the series-connected electrolytic column, so the column was operating with no hydrazine. No influence on the separation capacity of the two columns was observed at that time.About 20 hours after the failure had been initiated, hydrazine had degraded also in the first column und Pu(III) present in that column was reoxidized. During that time the Pu concentration in the organic raffinate of the first column increased very quickly from less than 1 mg Pu/l to above 500 mg Pu/l. However, in the second column Pu(IV) was reduced again to Pu(III) - which had been expected - and recycled to the first column together with the aqueous phase. The Pu concentration in the organic raffinate of the second column increased to a maximum of 1.7 mg Pu/l and reached a steady state concentration of 1 mg/l within the following 16 hours of the test. Plutonium accumulation in the top part of the first column attained peak values of 12 g Pu/l, measured in the aqueous phase. A simulation of this test with the VISCO computer code (8) yielded a similar development versus time with a maximum of 17 g Pu/l in the aqueous phase. Subsequently, the simulation yielded maximum Pu values of about 10 g/l. This test shows that even an extreme failure condition involving complete hydrazine degradation can be safely controlled by the interconnected system of two separate series-connected electrolytical columns. This finding can be explained by the fact that in the first column the nitric acid is extracted from the organic phase so that the acid concentration in the second column is lowered so much that Pu(III) can no longer be reoxidized by nitrite (9).

INFLUENCE OF TECHNETIUM ON U/PU SEPARATION

In some of the tests, technetium was added to the aqueous feed solution at different concentrations in order to investigate the influence of the latter on the stability of U/Pu separation and on the formation of side products (HN_3 and NH_4^+). The extraction of TcO_4^- into the organic phase was intensified by the addition of an approx. four-folderness of zirconium in order to feed to the partitioning column the greatest possible amount of technetium. In the partitioning column Tc(VII) is reduced very quickly to Tc(IV) in the presence of hydrazine and, along with Pu(III), backextracted into the aqueous phase (10). Precipitations of insoluable TcO_2 could not be observed.

Figure 9 shows the DF's for technetium in the uranium product (BXU) at different concentrations of $N_2H_5^+$ and Tc and the rates of hydrazine degradation and HN_3 as well as NH_4^+ formation, related to the plutonium throughput. These data show that major amounts of technetium remain in the organic uranium product only when no $H_2H_5^+$ is present. In the presence of $N_2H_5^+$, DF's for technetium of $>$ 100 are achieved.

$[N_2H_5^+]_{BXS}$ [M]	$[Tc]_{BSP}$ [mg/l]	Tc-DF for BXU	$\frac{\Delta N_2H_5^+}{Pu}$	$\frac{\Delta HN_3}{Pu}$	$\frac{\Delta NH_4^+}{Pu}$
0.2	290	>200	4.8	1.7	1.1
0.2	140	>150	3.5	1.7	0.3
0.1	5.5	--	2.2	<0.7	0.1
0.035	130	>100	1.9	1.3	0.2
0.035	0	--	0.65	<0.7	0.08
0	80	6.5	--	<0.7	0.1

org. feed : 85 to 92 gU+Pu/l, [U]/[Pu] $\sim$100, $[HNO_3] \sim 0.2$ M
strip solution : $[HNO_3] = 0.1$ M
Volume flow ratio org. /aq. in BX part : 5 to 7.25
cathodic current density : 0.5 to 0.8 mA/cm^2

Fig. 9: Hydrazine consumption and production of HN_3 and NH_4^+ in electroreduction BX column as function of hydrazine and Tc concentrations

The rate of $N_2H_5^+$ degradation depends, besides on the technetium concentration, also very much on the amount of hydrazine added, i. e. the lower the hydrazine concentration the slower the degradation, so thus the process is self-stabilizing. Also the HN_3 and NH_4 rates of formation are dependent both on the amount of $N_2H_5^+$ added and on the Tc concentration. When NH_4^+ is formed, the fraction which is produced by nitric acid reduction at the cathode (11) must be taken into account. This is evident from the tests performed in the absence of $N_2H_5^+$ and in the absence of technetium, respectively.

SUMMARY

U/Pu separation was greatly improved by electro-reduction. It appeared that the quality of dispersion is of crucial importance to the separation efficiency of the column. By optimization of the operating point in the flooding diagram decontamination factors for plutonium of greater than 10,000 were achieved.

By series connection of two electro-reduction columns the separation efficiency was clearly increased. DF's for plutonium of greater than 500,000 correspond were achieved, which meets the specification for the uranium final product.

The reliability of the process with a view to interferences in operation is markedly increased by the use of two series connected partitioning columns.

The stability of the process of electro-reduction is not disturbed by the presence of technetium. In order to minimize the formation of HN_3 the lowest possible hydrazine concentrations should be used. The addition of hydrazine can be dispensed with under selected flowsheet conditions but it results in higher Tc concentrations in the uranium product. With the results obtained a further important process step has been demonstrated towards implementing the one-cycle PUREX process.

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